Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ^{14}C

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[1] Many open questions exist about the importance of different sources of carbonaceous aerosol, which is a substantial contributor to the global aerosol budget and, therefore, to climate change and human mortality. In this work, ^{14}C was determined in elemental carbon (EC) and different organic carbon (OC) fractions from ambient urban aerosols with aerodynamic diameter <10 μm collected in Zurich (Switzerland). This enabled a more detailed source attribution of the carbonaceous aerosol mass than is possible with other currently available methods. The three major sources, fossil fuel, wood combustion (both anthropogenic emissions), and biogenic emissions, were quantified, making specific regulatory air quality management measures possible. EC originates nearly exclusively from fossil fuel usage during summer, whereas biomass-burning emissions become substantial during winter with ~25%, even though this source contributes only marginally to the local energy consumption. For OC, biogenic sources are dominant in summer with ~60%, where secondary organic aerosol prevails. Wood combustion accounts for up to ~41% of OC in winter. Fossil fuels represent ~30% of OC throughout the year.

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1. Introduction

[2] Fine aerosols are important for the Earth's climate by scattering and absorbing sunlight (direct effect) and by modifying cloud characteristics (indirect effect) [*Jacobson et al.*, 2000]. Furthermore, they have a negative impact on human health, as they contribute to respiratory and cardiopulmonary diseases and mortality [*Pope et al.*, 2002]. Carbonaceous particles are a major component of the fine aerosol. They originate from different anthropogenic and biogenic sources and are released as primary (i.e., directly emitted) particles or are formed as secondary organic aerosol (SOA) from volatile organic compounds (VOC) as gaseous precursors [*Jacobson et al.*, 2000]. Major anthropogenic emissions result from fossil fuel combustion and biomass burning. Biogenic carbonaceous aerosols mainly comprise plant debris, pollen, fungal spores, and bacteria as primary particles and SOA from biogenic VOC such as terpenes [*Hildemann et al.*, 1991; *Penner*, 1995; *Jacobson et al.*, 2000; *Andreae and Merlet*, 2001; *Bond et al.*, 2004; *Kanakidou et al.*, 2004]. For the identification and quantification of these sources, many elemental and organic molecular tracers have been employed, but their reliability often suffers from limited atmospheric lifetimes due to their chemical reactivity and highly variable emission factors. Thus there is a large uncertainty about the importance of anthropogenic emissions for the total carbonaceous aerosol burden of the atmosphere [*Penner*, 1995].

[3] In contrast to these tracers, radiocarbon (^{14}C) determinations offer a unique possibility for unambiguous source apportionment of carbonaceous aerosol particles [*Currie*, 2000]. This isotopic method enables a direct distinction of contemporary and fossil carbon in ambient aerosols, because ^{14}C has decayed in fossil material. $^{14}C/^{12}C$ ratios can be expressed as fractions of modern carbon (f_M). Values for f_M can range from 0 for fossil fuel sources to >1 for particles from the modern biosphere (see section 2.4), which makes possible an apportionment of anthropogenic and biogenic sources. However, widely used simple two-source models [e.g., *Currie*, 2000; *Currie et al.*, 1986, 1994; *Sheffield et al.*, 1994; *Lemire et al.*, 2002; *Lewis et al.*, 2004; *Szidat et al.*, 2004b] can only distinguish fossil from nonfossil emissions. Unfortunately, biomass-burning emissions, which should be assigned as anthropogenic, cannot be separated from bio-

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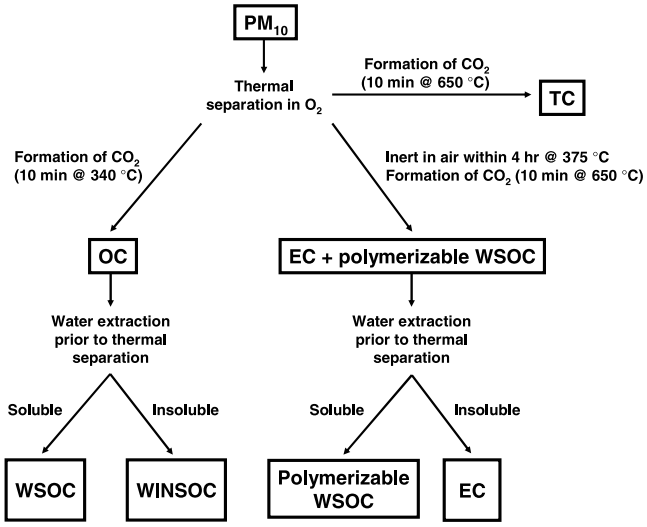

Figure 1. Separation scheme of the different carbon fractions. The ^{14}C was directly measured in OC, WINSOC, EC, and the mixture "EC + polymerizable WSOC." The ^{14}C values in WSOC and polymerizable WSOC were deduced from subtraction. Modified from *Szidat et al.* [2004c].

genic emissions by these simple models, as both sources contribute to the contemporary carbon fraction.

[4] Carbonaceous aerosol (total carbon, TC) is classified into the subfractions elemental carbon (EC) and organic carbon (OC) [*Jacobson et al.*, 2000]. The latter fraction can be divided further into water-insoluble OC (WINSOC), water-soluble OC (WSOC) [*Pun et al.*, 2000; *Mayol-Bracero et al.*, 2002; *Szidat et al.*, 2004c], and polymerizable WSOC (see section 2.2). This classification is widely acknowledged, although there is an ongoing debate on the optimum separation procedure of these method-dependent sum parameters [e.g., *Schmid et al.*, 2001]. EC is exceptional among all carbon fractions, because it is introduced to the atmosphere solely as primary particles either from fossil fuel combustion or from biomass burning. Consequently, f_M(EC) (i.e., f_M of the EC fraction) measurements allow a direct determination of the EC contributions from biomass and fossil fuel burning [*Klouda et al.*, 1990; *Currie et al.*, 2002; *Slater et al.*, 2002]. Moreover, they also enable an apportionment of fossil fuel, biomass-burning, and biogenic sources for OC using EC/OC emission ratios from biomass burning. In this work, direct $^{14}C/^{12}C$ measurements of individual fractions of the carbonaceous aerosol, especially OC and EC, were performed for source apportionment using a recently developed microanalytical technique [*Szidat et al.*, 2004c]. This new method goes far beyond the analysis of ^{14}C in TC alone, as often performed previously [e.g., *Currie et al.*, 1986, 1994; *Sheffield et al.*, 1994; *Lemire et al.*, 2002; *Lewis et al.*, 2004].

2. Methods

2.1. Aerosol Sampling

[5] At the urban background site Zurich (47°22′42″N, 8°31′52″E, 410 m a.s.l.) of the Swiss National Air Pollution Monitoring Network (NABEL) [*Swiss Federal Laboratories for Materials Testing and Research* (*EMPA*), 2000; *Gehrig and Buchmann*, 2003], aerosols were collected on quartz fiber filters (D = 150 mm, QF 20, Schleicher & Schuell) with a high-volume sampler (DA80, Digitel) and a PM_{10} inlet during 12 August to 8 September 2002 and 17 February to 26 March 2003 [*Szidat et al.*, 2004b, 2004c]. The station is situated in a parklike courtyard in the city center close to the main railway station. It is surrounded in the immediate vicinity by roads with rather low traffic as well as apartment buildings, small companies, and shops. The sampling sequences included daytime (usually between 8 a.m. and 8 p.m.), nighttime, and whole-day samples, representing 1–5 consecutive days.

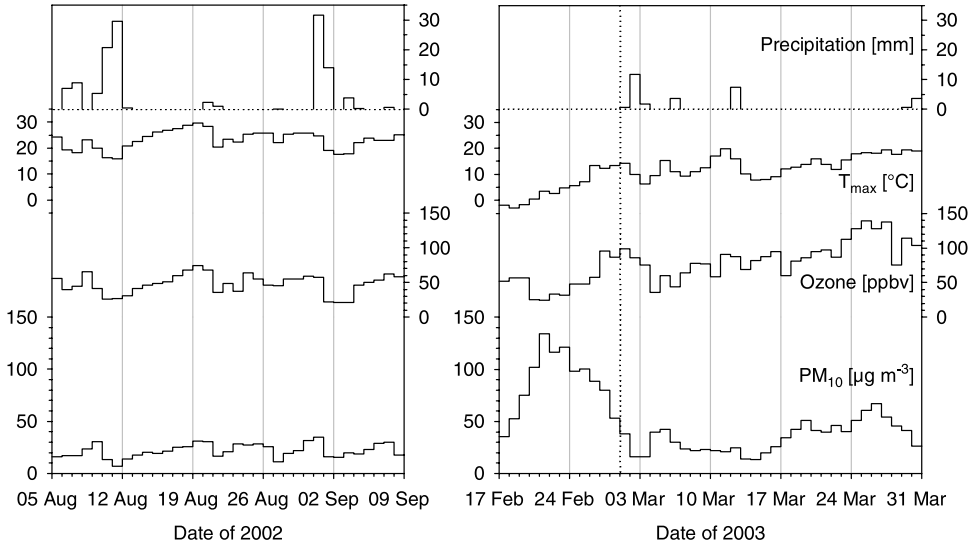

Figure 2. Meteorological parameters and concentrations of atmospheric components. Precipitation is given as daily depths, temperatures as well as ozone concentrations are given as daily maxima, and PM_{10} concentrations are given as daily means. The dotted vertical line on 1 March 2003 points out the transition from winter to springlike conditions.

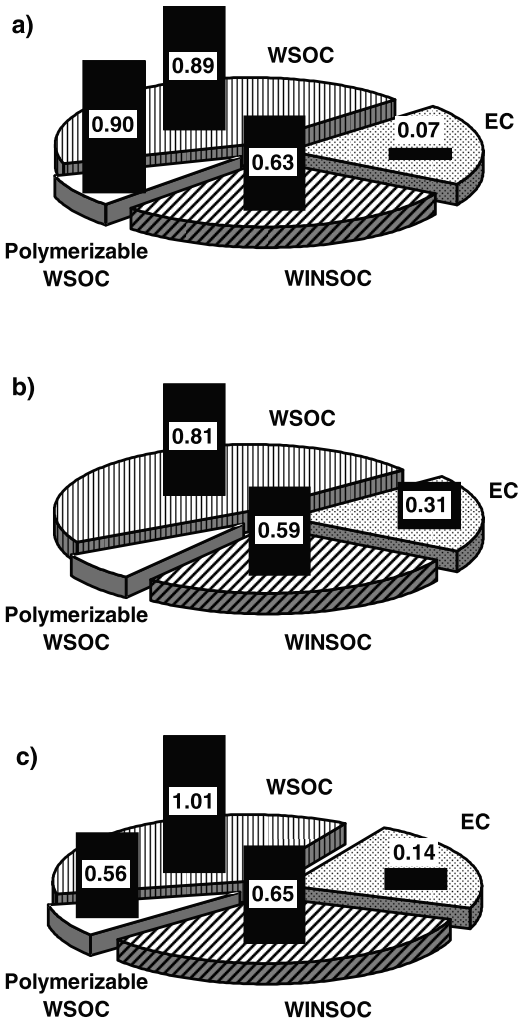

Figure 3. Typical composition of the carbonaceous aerosol (pies) and f_M values (bars and numbers) at Zurich for (a) summer, (b) winter, and (c) springlike conditions. The definition of the fractions of modern carbon (f_M) is given in section 2.4. Data refer to these samples: average of 16–21 and 21–26 August 2002 (Figure 3a), 19–21 February 2003 (Figure 3b), and average of 6–11 and 21–26 March 2003 (Figure 3c). The f_M(EC) for winter is given as average of 19–21 and 21–23 February 2003; the determination of f_M(polymerizable WSOC) for winter failed. The whole data set is shown in Figure 4. Note that total WSOC is composed of polymerizable WSOC and WSOC, as explained in section 2.2.

After sampling, filters were folded, wrapped in aluminum foil, packed into airtight plastic bags, and stored at −20°C until analysis.

2.2. Separation of Carbonaceous Particle Fractions

[6] In the system "Two-step heating system for the EC/OC determination of radiocarbon in the environment" (THEODORE), OC and EC were combusted from the filters in a stream of oxygen at 340°C and 650°C, respectively [*Szidat et al.*, 2004a]. The separation scheme for different carbonaceous particle fractions is given by *Szidat et al.* [2004c]. Figure 1 sketches this analytical procedure, which is briefly described in the following. OC was separated from other carbon fractions at 340°C. For the investigation of WINSOC, a water extraction was performed to remove WSOC prior to the thermal separation. The latter fraction was not analyzed directly, but determined by subtraction (WSOC = OC − WINSOC). Thermal elimination of OC for isolation of EC is susceptible to charring resulting in a positive artifact for the EC determination. Water extraction prior to thermal separation minimizes this artifact by elimination of the water-soluble fraction, and the difference in measured EC is then denoted polymerizable WSOC. The fact that polymerizable WSOC has a much higher f_M than EC (see below and in Figures 3 and 4) shows that the water extraction is important for EC isolation and does not result in an artifact removal of true EC. Note that the concentrations of this fraction were derived by subtraction as was done for WSOC (polymerizable WSOC = mixture "EC + polymerizable WSOC" − EC). Because of this fact, polymerizable WSOC is not a subfraction of WSOC, because the first was determined as the removed fraction within EC separation and the latter within OC separation. Thus both fractions sum up to the full water-soluble OC fraction.

2.3. Measurements of ^{14}C

[7] After combustion of the different carbonaceous particle fractions, evolving CO_2 was cryotrapped, determined manometrically, and transformed to filamentous carbon for $^{14}C/^{12}C$ determinations. These measurements were performed at the PSI/ETH compact accelerator mass spectrometry (AMS) system, which is based on a 500 kV pelletron accelerator [*Synal et al.*, 2000]. Details of the target production, measurement parameters, and data evaluation for submilligram samples are reported elsewhere [*Szidat et al.*, 2004a].

2.4. Definition of f_M

[8] f_M represents a $^{14}C/^{12}C$ ratio of a sample related to that present in the reference year 1950:

$$f_M = \frac{\left(^{14}C/^{12}C\right)_{sample}}{\left(^{14}C/^{12}C\right)_{AD1950}}. \quad (1)$$

Therefore fossil material is characterized by

$$f_{M,fossil} = 0. \quad (2)$$

[9] On the other hand, f_M should be 1 for contemporary samples because of this definition. However, materials from the last 50 years show values >1, with a maximum of ~2 in the early 1960s as a consequence of the nuclear bomb excess. This was shown by *Levin et al.* [2003] using time series of atmospheric $^{14}CO_2$. From these data, f_M for pure biogenic OC from 2002/2003 results as

$$f_{M,biogenic} = 1.072 \pm 0.015. \quad (3)$$

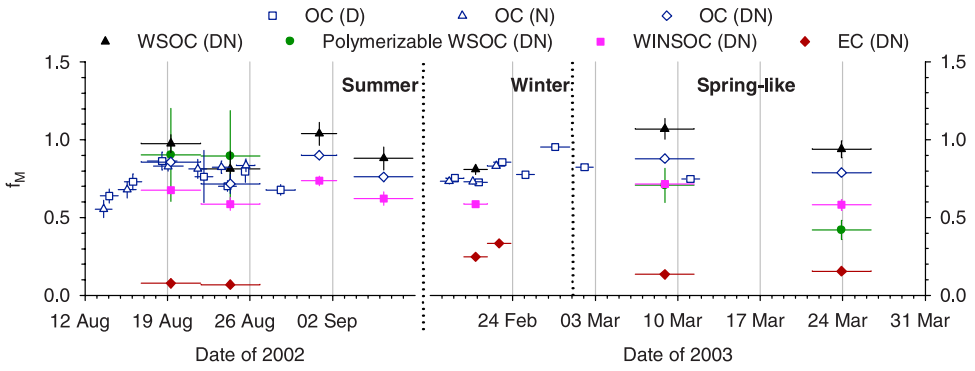

Figure 4. The f_M determinations of different carbon fractions with combined measurement uncertainties for daytime (D), nighttime (N), and whole-day (DN) samples. Horizontal bars mark beginning and end of aerosol collection.

[10] The uncertainty of $f_{M,biogenic}$ includes natural variability of $^{14}CO_2$ and a conservative estimation of the influence of primary biogenic OC, which could be older than the year of sampling. In accordance with *Lewis et al.* [2004],

$$f_{M,bb} = 1.24 \pm 0.05 \quad (4)$$

was set for biomass-burning (bb) contributions on the assumption that residential wood burning of 30–50-year-old softwood and hardwood was the major biomass-burning source for Zurich.

2.5. Determination of Organic and Inorganic Tracers

[11] Levoglucosan was determined in the aqueous extracts of the quartz fiber filters by HPLC with electrochemical detection (ED40, pulsed amperometry, gold working electrode). As eluent a sodium hydroxide gradient ranging from 30 to 40 mM was used. The eluent flow was 1 mL min^{-1}. The analytical column was a CarboPac PA 10. All instruments were from Dionex Corp. The detection limit of the method was 10 ng mL^{-1}. Field blanks for levoglucosan were negligible. The determination of cellulose combined enzymatic saccharification followed by enzymatic determination of the formed glucose and was performed according to the procedure given by *Puxbaum and Tenze-Kunit* [2003]. Potassium was measured with standard ion chromatography after water extraction of the filters and corrected for sea-salt and mineral dust contributions [*Szidat et al.*, 2004c]: non-sea-salt (nss) potassium and calcium was determined assuming constant K^+/Na^+ and Ca^{2+}/Na^+ ratios for sea salt of 0.0218 and 0.044, respectively; excess potassium (exK^+; i.e., potassium corrected for sea-salt and mineral dust contributions) was then calculated using the crustal average $nssK^+/nssCa^{2+}$ ratio of 0.71. The procedure to trace biomass-burning emissions using exK^+ benefits from K^+/Na^+ and K^+/Ca^{2+} ratios >10 for wood combustion [*Fine et al.*, 2001; *Schauer et al.*, 2001]. Isoprene and other trace gases were determined with gas chromatography–mass spectrometry (GC-MS). Biogenic isoprene denotes isoprene concentrations corrected for anthropogenic releases assuming a constant anthropogenic isoprene/1,3-butadiene mass ratio [*Reimann et al.*, 2000; *Szidat et al.*, 2004b].

3. Advanced Source Apportionment Model

3.1. General Results

[12] For February/March 2003, aerosol sampling began with a dry and cold period and a closed snow cover (Figure 2). During the first two weeks, an exceptional inversion episode dominated, with PM_{10} concentrations above 100 μg m^{-3}. This episode ended beginning of March 2003, when the weather turned to springlike conditions, and the snow cover has melted. During this month, PM_{10} concentrations reached an average value of about 30 μg m^{-3}, which were comparable to the level of August/September 2002. Consequently, the February/March 2003 campaign was divided into a winter (before 1 March) and a springlike

Table 1. Average Percentage Contributions of Different Sources to EC and OC for Summer, Winter, and Springlike Conditions for 2002/2003[a]

Source	Summer	Winter	Springlike
EC Fraction			
1. Anthropogenic emissions	~100	~100	~100
1.1. Biomass burning	6 ± 2	25 ± 5	12 ± 1
1.2. Fossil fuel usage	94 ± 2	75 ± 5	88 ± 1
2. Biogenic emissions	~0	~0	~0
OC Fraction			
1. Anthropogenic emissions	40 ± 10	73 ± 11 (±16)[b]	51 ± 5 (±10)[b]
1.1. Biomass burning	10 ± 2 (±4)[b]	41 ± 7 (±16)[b]	23 ± 2 (±8)[b]
1.2. Fossil fuel usage	31 ± 9	32 ± 8	28 ± 5
2. Biogenic emissions	60 ± 10	27 ± 11 (±19)[b,c]	49 ± 5 (±11)[b]

[a]Values plus or minus standard deviations between different samples of the same season are given, representing natural variations. Biomass burning was assumed as an anthropogenic source, thus neglecting natural wood fires, which is reasonable for western Europe [*Penner*, 1995; *Bond et al.*, 2004].

[b]In cases when the uncertainties of the advanced ^{14}C model for the single determinations were larger than the natural variability (mainly due to the uncertainty of $(EC/OC)_{ER,bb}$, see below in Table 3), these uncertainties are additionally shown in parentheses.

[c]For the discussion on the significance of $OC_{biogenic}$ in winter, see section 3.3.

Table 2. Determination of Tracers for Biomass Burning for Summer, Winter, and Springlike Conditions With Combined Measurement Uncertainties (1σ) or Detection Limits (95% Confidence)[a]

Sample	f_M(EC)	EC_{bb}, μg m^{-3}	Levoglucosan,[b] μg m^{-3}	exK^+, μg m^{-3}
16–21 August 2002	0.078 ± 0.029[c]	0.09 ± 0.02	0.09	0.10 ± 0.01
21–26 August 2002	0.070 ± 0.018	0.04 ± 0.01	0.05	<0.07
Summer average	0.073 ± 0.015[d]	0.06 ± 0.03[d]	0.07 ± 0.03	–
19–21 February 2003	0.248 ± 0.018	0.98 ± 0.23[c]	0.50[c]	0.44 ± 0.03
21–23 February 2003	0.334 ± 0.013	1.04 ± 0.37[c]	0.73[c]	–
Winter average	0.305 ± 0.058[d]	1.01 ± 0.20[d]	0.62 ± 0.16	–
6–11 March 2003	0.134 ± 0.005	0.14 ± 0.02	0.20	<0.08
21–26 March 2003	0.155 ± 0.003[c]	0.22 ± 0.03	0.25	<0.23
Springlike average	0.149 ± 0.013[d]	0.17 ± 0.06[d]	0.22 ± 0.04	–

[a]EC from biomass burning (EC_{bb}) was calculated according to equation (5).
[b]Typical uncertainties amount to 0.01 μg m^{-3}.
[c]Weighted mean of two measurements.
[d]Weighted average.

regime. The meteorological conditions during the summer campaign were already described previously [*Szidat et al.*, 2004b]. Briefly, this was a warm period with maximum temperatures of up to 30°C and sequences of several dry days followed by distinct precipitation events.

[13] Seasonally averaged f_M determinations of different carbon fractions are presented in Figure 3 (for f_M values of the whole data set, see Figure 4). The mean f_M(OC) amounted to 0.76 ± 0.09, 0.79 ± 0.08, 0.81 ± 0.05 for summer, winter, and springlike conditions, respectively. These averages are equal within uncertainties suggesting overall constant ratios of emission sources independent of the season. This result is unexpected, as the contemporary carbon content is supposed to be lower for winter because of reduced SOA formation from biogenic gaseous precursors as well as reduced biogenic primary emissions [*Tsigaridis and Kanakidou*, 2003], and will be explained below.

3.2. Source Apportionment of EC

[14] Concentrations of EC originating from biomass burning (EC_{bb}) were deduced from f_M(EC) by

$$EC_{bb} = EC_{tot} \cdot \frac{f_M(EC)}{f_{M,bb}}, \quad (5)$$

where EC_{tot} is the concentration of total EC. Consequently, the concentration of EC from fossil sources (EC_{fossil}), is given by

$$EC_{fossil} = EC_{tot} - EC_{bb} = EC_{tot} \cdot \left(1 - \frac{f_M(EC)}{f_{M,bb}}\right). \quad (6)$$

[15] The contribution of biomass burning to EC is then EC_{bb} divided by EC_{tot} and amounts to 6 ± 2%, 12 ± 1%, and 25 ± 5% during summer, springlike, and winter conditions, respectively (Table 1). Therefore EC was dominated by fossil emission sources, in contrast to OC (see above). The higher fraction of biomass burning for winter was corroborated by measurements of potassium and levoglucosan (Table 2), two widely used tracers for biomass burning [*Sheffield et al.*, 1994; *Andreae and Merlet*, 2001; *Nolte et al.*, 2001]: levoglucosan and EC_{bb} concentrations showed similar seasonal variations with average summer/winter ratios of 0.11 and 0.06, respectively. Note that these ratios become 0.49 and 0.26, respectively, if normalized to the PM_{10} concentrations, because of the highly elevated PM values during the inversion episode in winter. However, levoglucosan emission factors may vary by a factor of 5 or higher [*Andreae and Merlet*, 2001; *Nolte et al.*, 2001], resulting in large uncertainties for source apportionment (see also Table 3). The potential of potassium as biomass-burning tracer is limited as well because of interferences from mineral dust [see also *Szidat et al.*, 2004c]. Thus these two conventional tracers lack the accuracy of ^{14}C for the source apportionment of EC because of the variability of emission ratios.

3.3. Source Apportionment of OC

[16] For source apportionment of OC, an advanced model is applied to discriminate between biomass-burning and biogenic emissions within the contemporary carbon fraction (Figure 5). The biomass-burning fraction of OC (OC_{bb}) is

Table 3. Literature Data of Emission Ratios of EC/OC $(EC/OC)_{ER,bb}$ and Levoglucosan/OC $(lev/OC)_{ER,bb}$ Determined From Average Emission Factors for Residential Burning (Fireplaces) of Softwood and Hardwood[a]

$(EC/OC)_{ER,bb}$	$(lev/OC)_{ER,bb}$	Reference
0.175	–[b]	*Edgerton et al.* [1986]
0.163	–	*Rau* [1989]
0.084	–	*Hildemann et al.* [1991]
0.116	–	*Cachier et al.* [1996]
0.234	–	*Liousse et al.* [1996]
0.182	–	*McDonald et al.* [2000]
0.153	0.103	*Fine et al.* [2001]
(0.040)[a,c]	0.246[a]	*Schauer et al.* [2001]
0.159[a]	0.042[a]	*Fine et al.* [2002]
0.086[a]	0.134[a]	*Fine et al.* [2004a]
0.213	0.245	*Fine et al.* [2004b]
0.16 ± 0.05	0.15 ± 0.09	average

[a]Values are given only for wood species that are representative for Switzerland, i.e., spruce, fir, hemlock, pine, beech, maple, birch, and oak.
[b]Dash means that $(lev/OC)_{ER,bb}$ was not reported in this study.
[c]Value is not considered for the average, as it was detected as an outlier by the Grubbs test (based on logarithmic ratios, 95% level of confidence).

estimated from EC_{bb} using an average EC/OC emission ratio $(EC/OC)_{ER,bb}$:

$$OC_{bb} = \frac{EC_{bb}}{\left(EC/OC\right)_{ER,bb}} = \frac{EC_{tot}}{\left(EC/OC\right)_{ER,bb}} \cdot \frac{f_M(EC)}{f_{M,bb}}. \quad (7)$$

Table 3 shows that $(EC/OC)_{ER,bb}$ amounts 0.16 ± 0.05 for residential wood burning of softwood and hardwood in fireplaces, which we assume as the major source of biomass burning in Switzerland and western Europe. Excess contemporary OC is defined as biogenic OC ($OC_{biogenic}$), comprising primary and secondary components:

$$OC_{biogenic} = \frac{OC_{tot} \cdot f_M(OC) - OC_{bb} \cdot f_{M,bb}}{f_{M,biogenic}} = \frac{OC_{tot} \cdot f_M(OC) - \frac{EC_{tot}}{\left(EC/OC\right)_{ER,bb}} \cdot f_M(EC)}{f_{M,biogenic}}, \quad (8)$$

where OC_{tot} is the total OC concentration. The concentration of fossil OC (OC_{fossil}) is then

$$\begin{aligned} OC_{fossil} &= OC_{tot} - OC_{bb} - OC_{biogenic} \\ &= OC_{tot} - \frac{EC_{tot}}{\left(EC/OC\right)_{ER,bb}} \cdot \frac{f_M(EC)}{f_{M,bb}} \\ &\quad - \frac{OC_{tot} \cdot f_M(OC) - \frac{EC_{tot}}{\left(EC/OC\right)_{ER,bb}} \cdot f_M(EC)}{f_{M,biogenic}} \\ &= OC_{tot} \cdot \left(1 - \frac{f_M(OC)}{f_{M,biogenic}}\right) \\ &\quad + \frac{EC_{tot}}{\left(EC/OC\right)_{ER,bb}} \cdot f_M(EC) \cdot \left(\frac{1}{f_{M,biogenic}} - \frac{1}{f_{M,bb}}\right). \end{aligned} \quad (9)$$

Finally, $OC_{anthropogenic}$ is defined as sum of all man-made emissions:

$$OC_{anthropogenic} = OC_{fossil} + OC_{bb}. \quad (10)$$

[17] As the uncertainty of $(EC/OC)_{ER,bb}$ has a large impact on the combined standard uncertainties of OC_{bb}, $OC_{anthropogenic}$, and $OC_{biogenic}$, the values in Table 3 will be discussed in detail in the following. (Note that the uncertainty of $(EC/OC)_{ER,bb}$ has only little influence on the uncertainty of OC_{fossil} and no influence on the ones of EC_{bb} and EC_{fossil}.) The relative standard deviation (r.s.d.) of $(EC/OC)_{ER,bb}$ of 32% comprises two main components of uncertainty among the studies listed in Table 3: wood burning conditions and procedures of the OC/EC determination. Especially, the use of literature data from different OC/EC separation methods always has to be considered carefully [*Schmid et al.*, 2001], and it is not clear how much this method-dependent variability contributes to the uncertainty of $(EC/OC)_{ER,bb}$. Therefore the significant outlier in Table 3 may have been caused by substantially deviating methods. Within Table 3, some older data [e.g., *Dasch*, 1982] were not considered, when direct sampling of combustion aerosols was conducted without dilution with clean air, as this procedure does not reflect ambient atmospheric conditions [*Bond et al.*, 2004]. Moreover, Table 3 does not account for waste burning. Agricultural, forestry, and private waste fires of wood have a certain occurrence in Switzerland (see Tables 6 and 7), but they are supposed to occur mainly in April/May and September-November [*Liousse et al.*, 1996]. Especially in the end of February 2003, when a large contribution of EC_{bb} was observed, substantial activities of open-field waste burning of wood are very unlikely because of the low temperatures and the closed snow cover. Particle emissions of waste incineration facilities, on the other hand, are very small compared to the total burden in Switzerland (Tables 6 and 7). Consequently, the impact of all these sources on this work can be neglected.

[18] For validation of the advanced source apportionment model sketched in Figure 5, OC_{bb} concentrations as obtained from equation (7) are compared in Table 4 with $OC_{bb,lev}$ derived from levoglucosan (lev) concentrations using

$$OC_{bb,lev} = \frac{lev}{\left(lev/OC\right)_{ER,bb}}, \quad (11)$$

where $(lev/OC)_{ER,bb}$ is the average levoglucosan to OC emission ratio from residential wood burning of softwood and hardwood in fireplaces. This ratio amounts 0.15 ± 0.09 (Table 3), representing a smaller number of studies and a larger variation of results than $(EC/OC)_{ER,bb}$. The differences between OC_{bb} and $OC_{bb,lev}$ are insignificant for all seasons, but the uncertainties for the single determinations are high because of the uncertainties of both emission ratios. It would be interesting to see if the discrepancy between OC_{bb} and $OC_{bb,lev}$ during winter is real, possibly due to seasonal variations of emissions and atmospheric lifetimes for levoglucosan and EC_{bb}. This analysis is however not possible on the basis of the current data set and needs more investigation. However, results from Table 4 serve as an independent quality control for the advanced ^{14}C model and the outcome of Table 1, because the determinations of OC_{bb} according to equations (7) and (11) are based on independent tracers.

[19] Table 1 summarizes average contributions of OC from anthropogenic (separated for biomass burning and fossil fuel usage) and biogenic emissions for summer, winter, and springlike conditions. While anthropogenic emissions dominate the OC concentration in winter with ~73%, biogenic emissions are the largest source in summer with a contribution of ~60%. The contribution of biomass burning follows a seasonal trend as well, varying from ~10% for warm to ~41% for cold periods. In contrast, the fossil fuel contribution, ~30%, is quite independent of

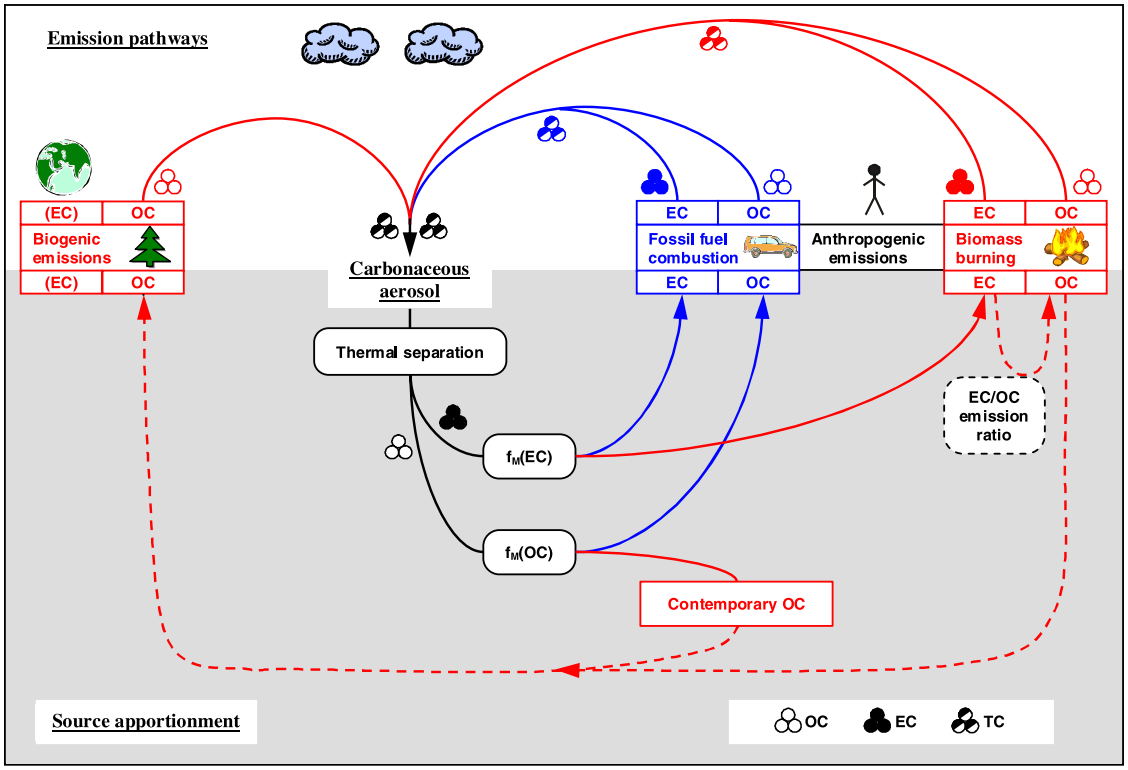

Figure 5. Main emission pathways of carbonaceous aerosol fractions OC, EC, and TC and their source apportionment according to the advanced ^{14}C model used in this study. Source patterns of the different fractions are distinguished between fossil carbon (blue), contemporary carbon (red), and mixtures of both (black). Dashed lines indicate supplements of the advanced source apportionment model to often employed inappropriate simple two-source ^{14}C models. Biomass burning was assumed as an anthropogenic source, thus neglecting naturally occurring wood fires as a biogenic EC source (see Table 1).

season, resulting in a constant average $f_M(OC)$ for winter, springlike, and summer conditions.

[20] There is a high correlation between OC_{fossil} and EC_{tot} with nearly the same slope in summer and winter (with $OC_{fossil} = 1.2 \times EC_{tot}$ and $R^2 = 0.84$, see Figure 6). Various authors [e.g., *Castro et al.*, 1999; *Lim and Turpin*, 2002] made use of this by interpreting the lowest OC to EC ratios (i.e., OC_{tot}/EC_{tot} according to our nomenclature) in such a correlation as the constant primary OC to EC ratio. In that approach, winter data are often used in order to neglect biogenic SOA. However, our results show that winter aerosol may be influenced by biomass-burning emissions, which cannot be detected by OC/EC determinations without isotopic information. Therefore the approach of a constant primary OC to EC ratio is only justified in the absence of biomass-burning emissions, which has to be evaluated carefully. The correlation between OC_{fossil} and EC_{fossil} indicates a similar relation (with $OC_{fossil} = 1.5 \times EC_{fossil}$ and $R^2 = 0.80$, see Figure 7). The quality of the correlation shown in Figure 7 is identical to that of Figure 6 on the basis of an F test of both standard deviations about regression (95% confidence). Thus the quality of correlation between OC_{fossil} and EC_{tot} was not significantly biased by the biomass-burning contribution of 25% within EC_{tot} during winter. On the other hand, both slopes are significantly different on the basis of a t test (95% confidence). The value of Figure 7 may give a realistic estimation of an ambient OC/EC ratio from fossil fuel sources including the influence of different emission patterns and atmospheric sinks.

[21] The OC fraction from biogenic emissions amounts to ~27% for winter. Unfortunately, only 2 winter samples showed significant fractions of $OC_{biogenic}$ applying equation (8), while the remaining 6 samples revealed a value

Table 4. Estimations of Biomass-Burning OC as Deduced From EC_{bb} Using Equation (7) and From Levoglucosan Concentrations Using Equation (11)

Sample	OC_{bb} (From EC_{bb}), $\mu g\ m^{-3}$	$OC_{bb,lev}$ (From Levoglucosan), $\mu g\ m^{-3}$
16–21 August 2002	0.5 ± 0.2	0.6 ± 0.3
21–26 August 2002	0.2 ± 0.1	0.3 ± 0.2
Summer average	0.3 ± 0.1[a]	0.4 ± 0.2[a]
19–21 February 2003	6.7 ± 3.0[b]	3.3 ± 1.9[b]
21–23 February 2003	7.1 ± 3.2[b]	4.7 ± 2.8[b]
Winter average	6.9 ± 3.1[a]	3.7 ± 2.2[a]
6–11 March 2003	0.9 ± 0.4	1.3 ± 0.7
21–26 March 2003	1.5 ± 0.6	1.6 ± 1.0
Springlike average	1.1 ± 0.5[a]	1.4 ± 0.8[a]

[a]Weighted average.
[b]Weighted mean of two measurements.

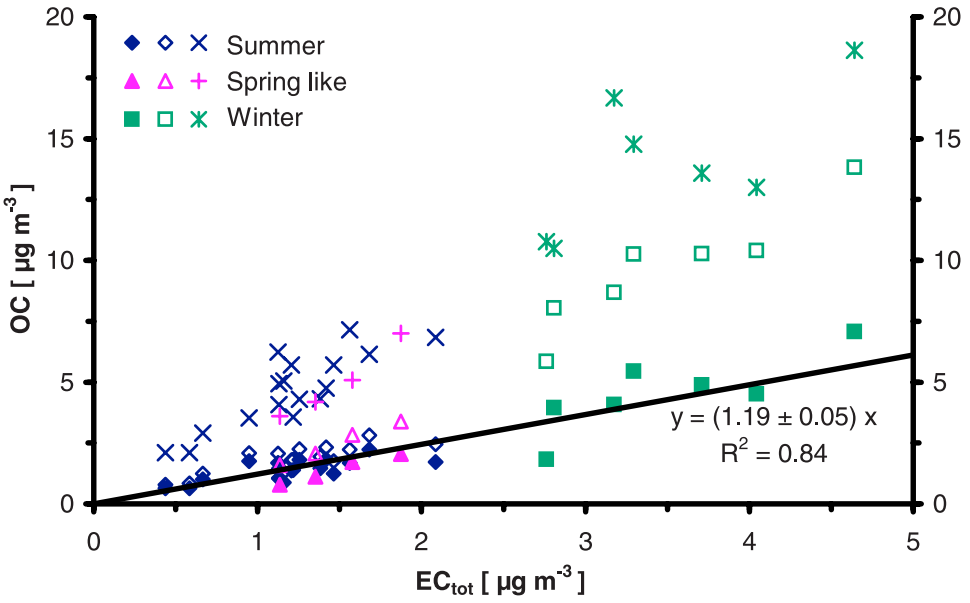

Figure 6. Total OC (OC_{tot}; crosses), anthropogenic OC (representing OC_{fossil} and OC_{bb}; open symbols), and fossil OC (OC_{fossil}; solid symbols) concentrations as a function of total EC (EC_{tot}) concentrations for summer, springlike, and winter conditions. The correlation of OC_{fossil} and EC_{tot} is within uncertainties identical for all seasons, with an overall OC_{fossil} to EC_{tot} ratio of 1.19 ± 0.05.

below detection limit (95% confidence), which was caused by the high uncertainty of $(EC/OC)_{ER,bb}$. Thus the abundance of OC from biogenic sources during winter needs further confirmation. However, $OC_{biogenic}$ was significantly detected in all samples under springlike conditions. Cellulose measurements reveal that organic matter comprises only 2, 5 and 6% primary particles from plant debris for summer, winter and springlike conditions, respectively (Table 5). This suggests that SOA from biogenic VOC precursors remains as a major source for the high biogenic OC fraction even in winter (see below). These findings are reflected in the f_M values for WSOC, which were ~50% higher than for WINSOC for all seasons (Figure 3). In summer, WSOC is mainly attributed to SOA [*Pun et al.*, 2000; *Kanakidou et al.*, 2004]. Consequently, high f_M(WSOC) values suggest that biogenic SOA exceeds anthropogenic SOA by far even in the urban environment of Zurich for this season. In winter on the other hand, water-soluble products from biomass burning [*Mayol-Bracero et al.*, 2002] contribute substantially to the high f_M(WSOC) values.

4. Atmospheric Relevance

[22] The sum of evidence confirms that the higher anthropogenic contribution to OC during winter is caused by elevated biomass-burning emissions, which exceeds fossil fuel emissions in this season. This is remarkable, as the total energy consumption in Switzerland for 2003 comprised only 2.6% from wood burning compared to 70.2% from combustion of fossil fuels [*Swiss Federal Office of Energy* (*BFE*), 2004]. However, for a correct interpretation of these numbers one should keep in mind the different emission factors and energy efficiencies of these fuels [*Swiss Federal Office of Energy* (*BFE*), 2004; *Bond et al.*, 2004]: biomass burning results in approximately 4 times and 80 times larger emissions of carbonaceous particles than operating diesel and gasoline vehicles, respectively, if related to the same

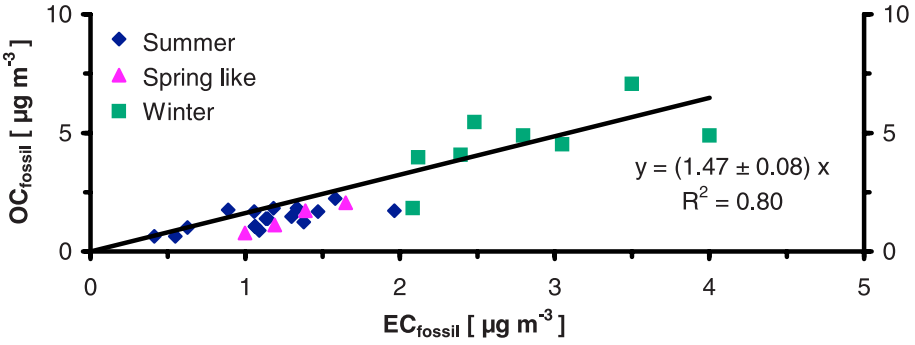

Figure 7. OC_{fossil} concentrations as a function of EC_{fossil} concentrations for summer, springlike, and winter conditions with an overall OC_{fossil} to EC_{fossil} ratio of 1.47 ± 0.08.

Table 5. Primary Biogenic Emissions for Summer, Winter, and Springlike Conditions

Sample	Cellulose,[a] μg m^{-3}	Plant Debris/OM,[b] %	Plant Debris/Biogenic OM,[b] %
16–21 August 2002	0.06	1.3	2
21–26 August 2002	0.06	2.7	5
Summer average	0.06	2.0	3
19–21 February 2003	0.49[c]	3.6[c]	15[c]
21–23 February 2003	0.82[c]	6.2[c]	19[c]
Winter average	0.66	4.9	17
6–11 March 2003	0.22	7.6	14
21–26 March 2003	0.24	4.3	9
Springlike average	0.23	5.9	11

[a]Typical uncertainties amount to 0.01 μg m^{-3}.
[b]Plant debris was calculated from cellulose using a scaling factor of 2, and organic matter (OM) was calculated from OC using a scaling factor of 1.6 [*Puxbaum and Tenze-Kunit*, 2003]. Percentages are mass related.
[c]Mean of two measurements.

amount of thermal energy gained by these combustion processes. These circumstances give rise to the high fraction of biomass-burning aerosols during the heating period as observed. Similar results were suggested by *Bond et al.* [2004] using inventory-based model calculations: that study yielded ~15% biomass-burning contribution to total EC for Europe, which may lead to a similar value for OC. Unfortunately, their calculations suffer from large uncertainties (e.g., 100% for residential wood burning) and a neglect of seasonal effects. Furthermore, they report that their model tends to significantly underpredict observed EC concentrations [*Bond et al.*, 2004].

[23] For comparison of the results in Table 1, inventory-based EC emissions were calculated for Switzerland and the Canton of Zurich in Tables 6 and 7, respectively. For that, we used the PM_{10} emission data submitted to the UN-ECE Convention on Long-Range Transboundary Pollution, and applied two different data sets of emission ratios $(EC/PM_{10})_{ER}$. Finally, EC_{bb} and EC_{fossil} emissions were calculated as annual masses and percentages related to EC_{tot}. Concerning the seasonality we used typical weighting factors for all emission classes. For simplicity, we assumed identical lifetimes of all components given in Tables 6 and 7 so that ratios of different source strengths translate into equal concentration ratios under ambient atmospheric conditions, which is necessary for comparison with the results of Table 1. It is important to note that the ranges of results in Tables 6 and 7 only represent the differences of the two sets of emission ratios. Neither uncertainties within one of these data sets, nor those of the original PM_{10} emission data are reflected. Both additional uncertainties can be very high (e.g., as mentioned above) thus allowing only a qualitative comparison with Table 1. For OC, these uncertainties exceeded 100% by far especially for noncombustion sources so that we refrained from estimating inventory-based emissions for this fraction. Recent publications followed the same strategy: *Schaap et al.* [2004] did not consider OC at all, and *Bond et al.* [2004] only allowed for OC emissions

Table 6. EC Emissions of Switzerland for 2000 Based on Swiss PM_{10} Emission Data Submitted in 2005 to the UNECE Convention on Long-Range Transboundary Pollution and on Two Different Sets of $(EC/PM_{10})_{ER}$[a]

	Annual Sum (Days 1–365)		Winter Months (Days 30–59)			Summer Months Days (224–253)		
Source	Gg yr^{-1}	Percent	wf	Gg (30 d)$^{-1}$	Percent	wf	Gg (30 d)$^{-1}$	Percent
Wood (heating)	0.23[b]–0.41[c]	6[b]–11[c]	0.164	0.04[b]–0.07[c]	12[b]–22[c]	0	0[b,c]	0[b,c]
Wood (waste burning)[d]	0.26[b]–0.45[c]	7[b]–12[c]	0	0[b,c]	0[b,c]	0.05	0.01[b]–0.02[c]	5[b]–9[c]
Fossil fuel (heating)	0.05[b]–0.10[c]	1[b]–3[c]	0.164	0.01[b]–0.02[c]	3[b]–5[c]	0	0[b,c]	0[b,c]
Traffic (exhaust)[e]	2.36[c]–2.82[b]	63[c]–74[b]	0.082	0.20[c]–0.23[b]	62[c]–74[b]	0.082	0.20[c]–0.23[b]	77[c]–83[b]
Traffic (nonexhaust)[e,f]	0.43[b,c]	11[b]–12[c]	0.082	0.04[b,c]	11[b,c]	0.082	0.04[b,c]	13[b]–14[c]
EC_{bb}	0.50[b]–0.87[c]	13[b]–23[c]	–	0.04[b]–0.07[c]	12[b]–22[c]	–	0.01[b]–0.02[c]	5[b]–9[c]
EC_{fossil}	2.88[c]–3.31[b]	77[c]–87[b]	–	0.25[c]–0.28[b]	78[c]–88[b]	–	0.23[c]–0.27[b]	91[c]–95[b]
EC_{tot}	3.75[c]–3.80[b]	100	–	0.32[b,c]	100	–	0.25[c]–0.28[b]	100

[a]Data submitted to United Nations Economic Commission for Europe (UNECE) convention are from R. Quartier (private communication, 2005); a previous estimation for the year 1995 is given by *Swiss Agency for the Environment, Forests and Landscape* [BUWAL] [2001]. Results for winter and summer conditions are calculated with weighting factors (wf) representing the seasonal relevance of the sources as given by *Liousse et al.* [1996] for residential heating and waste burning of wood and under the assumption that traffic emissions are constant throughout the year. Note that data ranges only indicate differences of the two sets of emission ratios and do not reflect uncertainties within these data sets and those of the Swiss PM_{10} emission data.
[b]Values estimated using these $(EC/PM)_{ER}$: Table 3 for wood (heating and waste burning) under the assumption that particulate emissions completely consist of TC (in accordance, e.g., with *Schauer et al.* [2001] and *Fine et al.* [2001, 2004a]), *Bond et al.* [2004] for fossil fuel (heating) and traffic (exhaust), and *Hildemann et al.* [1991] for traffic (nonexhaust). Note that *Bond et al.* [2004] use a data set similar to Table 3 for the evaluation of EC inventories from residential wood combustion.
[c]Values estimated using these $(EC/PM)_{ER}$: *Schaap et al.* [2004] for wood (heating and waste burning), fossil fuel (heating), and traffic (exhaust) and *Hildemann et al.* [1991] for traffic (nonexhaust).
[d]Wood (waste burning) comprises mainly forestry (~60%), agricultural (~20%), and private garden (~15%) activities. Fossil and biomass EC emissions from waste incineration facilities can be neglected (<3%).
[e]Emissions from traffic consider road, air, and rail transport as well as agricultural and construction vehicles.
[f]Traffic (nonexhaust) comprises mainly road (~65%) and tire (~30%) abrasion.

Table 7. Same as Table 6, but for the Canton of Zurich[a]

Source	Annual Sum (Days 1–365)		Winter Months (Days 30–59)			Summer Months (Days 224–253)		
	Mg yr^{-1}	Percent	wf	Mg (30 d)$^{-1}$	Percent	wf	Mg (30 d)$^{-1}$	Percent
Wood (heating)	19[b]–35[c]	3[b]–6[c]	0.164	3.2[b]–5.9[c]	6[b]–12[c]	0	0[b,c]	0[b,c]
Wood (waste burning)[d]	29[b]–51[c]	5[b]–9[c]	0	0[b,c]	0[b,c]	0.05	1.5[b]–2.6[c]	3[b]–6[c]
Fossil fuel (heating)	1[b]–2[c]	<1[b,c]	0.164	0.2[b]–0.3[c]	<1[b,c]	0	0[b,c]	0[b,c]
Traffic (total)[e]	492[c]–584[b]	11[b]–12[c]	0.082	40.9[c]–48.5[b]	87[b]–94[c]	0.082	40.9[c]–48.5[b]	94[b]–97[c]
EC_{bb}	49[b]–86[c]	8[b]–15[c]	–	3.2[b]–5.9[c]	6[b]–12[c]	–	1.5[b]–2.6[c]	3[b]–6[c]
EC_{fossil}	494[c]–585[b]	85[c]–93[b]	–	41.2[c]–48.6[b]	88[c]–84[b]	–	40.9[c]–48.5[b]	94[b]–97[c]
EC_{tot}	581[c]–634[b]	100	–	47.1[c]–51.8[b]	100	–	43.4[c]–49.9[b]	100

[a]H. Sommer (private communication, 2005).

[b]Values estimated using these $(EC/PM)_{ER}$: Table 3 for wood (heating and waste burning) under the assumption that particulate emissions completely consist of TC (in accordance, e.g., with *Schauer et al.* [2001] and *Fine et al.* [2001, 2004a]), *Bond et al.* [2004] for fossil fuel (heating) and traffic (exhaust), and *Hildemann et al.* [1991] for traffic (nonexhaust). Note that *Bond et al.* [2004] use a data set similar to Table 3 for the evaluation of EC inventories from residential wood combustion.

[c]Values estimated using these $(EC/PM)_{ER}$: *Schaap et al.* [2004] for wood (heating and waste burning), fossil fuel (heating), and traffic (exhaust) and *Hildemann et al.* [1991] for traffic (nonexhaust).

[d]Wood (waste burning) comprises mainly forestry (∼25%), agricultural (∼15%), and private garden (∼60%) activities. Fossil and biomass EC emissions from waste incineration facilities can be neglected (<1%).

[e]Emissions from traffic consider road, air, and rail transport as well as agricultural and construction vehicles assuming the same percentages of traffic (exhaust) and traffic (nonexhaust) within traffic (total) as for Switzerland (Table 6).

from combustion sources, but neglected other emission pathways. Consequently, these models cannot provide a source attribution of the entire carbonaceous aerosol mass.

[24] The comparison of the ^{14}C-deduced contribution of EC_{bb} in Table 1 with inventory-based estimations in Tables 6 and 7 show a high consistency for summer conditions with nearly exclusive emissions from traffic. For winter, results for EC_{bb} in Table 1 accord with the upper inventory-based estimate for Switzerland from Table 6, which mainly utilizes the emission ratios of *Schaap et al.* [2004]. The values of *Bond et al.* [2004] lead to lower EC emissions. The large difference between both data sets evolves mainly from the evaluation of $(EC/PM_{10})_{ER}$ for biomass burning, which, in fact, was identified as the most important uncertainty by *Bond et al.* [2004]. On the other hand, the proportion of EC_{bb} for winter from Table 1 is higher than both estimates for the Canton of Zurich (Table 7). As already stated earlier [*Szidat et al.*, 2004b, 2004c], aerosols collected at the NABEL station Zurich do not show a typical local (urban), but more a regional (rural) signal. This was underlined by *Gehrig and Buchmann* [2003]. They observed high correlations of PM_{10} concentrations between different NABEL stations in the lowlands of the Swiss basin and concluded that meteorological conditions and emissions from sources, which are effective over the whole area, dominate the relative variations of the concentrations of fine dust rather than specific local sources and events. Therefore one can hardly assess, whether the inventory of the Canton of Zurich (its area ends only ∼10 km upwind from the sampling site for the main, i.e., western wind direction) or the average Swiss inventory is relevant. In conclusion, the comparison of results from Table 1 with inventory-based emissions suggests general agreement for EC with a possible discrepancy for winter, which remains unexplained.

[25] Chemical mass balance (CMB) models using organic tracer compounds are also applied to relate ambient particle mass to emission sources. However, they often yield conflicting results and/or a large fraction of unexplained mass (see Table 8). The latter can amount to 75% and is mainly attributed to unknown SOA sources. Thus CMB models are often not able to assign a major fraction of the organic aerosol mass to anthropogenic or biogenic sources. Therefore $^{14}C/^{12}C$ measurements of OC and EC can provide input data for refined inventory-based and CMB model estimations by unambiguously assigning the whole OC mass fraction to anthropogenic or biogenic sources.

[26] Model results generally agree with our findings concerning biogenic emissions in summer: global model calculations by *Tsigaridis and Kanakidou* [2003] and estimations based on $f_M(TC)$ determinations [*Lewis et al.*, 2004] suggested a dominant biogenic contribution. The regional three-dimensional Eulerian model CAMx4 [*Andreani-Aksoyoglu et al.*, 2004] attributes at least 60% of total SOA to biogenic precursors for Zurich during August 2003 as well (S. Andreani-Aksoyoglu, private communication, 2005). In contrast, the modeled biogenic contribution to SOA appears to be underestimated in winter [*Tsigaridis and Kanakidou*, 2003], despite of the fact that emission inventories demonstrate substantial emissions of terpenes even during this season [*Andreani-Aksoyoglu and Keller*, 1995]. A possible reason for underpredicting SOA

Table 8. Chemical Mass Balance Modeling of Particulate Organic Carbon in the Literature[a]

Sources	A	B	C	D	E
1. Total fossil carbon sources	**17**	**48**	**33**	**17**	**85**
1.1. Fossil fuel combustion	17	40	32	13	81
1.2. Road dust, tire wear debris	–	8	1	4	4
2. Total contemporary carbon sources	**83**	**37**	**27**	**7**	**14**
2.1. Biomass burning	48[b]	16	17	5	8
2.2. Biogenic (vegetation debris)	–	1	–	2	–
2.3. Meat cooking	–	17	10	–	6
2.4. SOA from terpenes	35	–	–	–	–
3. Unexplained (not identified) sources	–	**21**	**31**	**76**	**<1**

[a]Values are given as percentage of measured OC concentrations. Results originate from the following studies: A, average for United States, large regional differences observed [*Park et al.*, 2003]; B, average of downtown Los Angeles and Pasadena, urban [*Schauer et al.*, 1996]; C, Bakersfield, urban [*Schauer and Cass*, 2000]; D, five urban sites in southern California, average of three seasons [*Manchester-Neesvig et al.*, 2003]; E, average of nine sites from urban to rural [*Watson et al.*, 1998].

[b]Value is divided into 19% biomass burning and 29% biofuel combustion.

may be missing biogenic sources such as isoprene [*Claeys et al.*, 2004a], which globally accounts for about half of the emitted VOC emissions [*Tsigaridis and Kanakidou*, 2003]. It has until recently not been considered as a major SOA precursor, however, the mechanism proposed by *Claeys et al.* [2004b] as well as the polymerization mechanism proposed by *Kalberer et al.* [2004] would both result in a higher biogenic SOA fraction. Biogenic isoprene [*Reimann et al.*, 2000] has been measured in this study and was found to be 19^{+20}_{-10}, 17^{+18}_{-9}, and 52^{+23}_{-16} pptv (geometric means with standard deviations) on average for winter, springlike, and summer conditions, respectively. (Note that the VOC concentrations for winter were elevated by a factor of ~1.7 based on 1,3-butadiene measurements due to the inversion condition.) These values demonstrate the importance of biogenic SOA precursors during summer, but also the presence of a nonnegligible biological activity during winter, suggesting the formation of biogenic SOA also for that time period.

5. Conclusions

[27] We analyzed $^{14}C/^{12}C$ ratios in terms of fractions of modern carbon (f_M) in total organic carbon (OC), water-insoluble OC (WINSOC), and elemental carbon (EC) of urban background aerosols from Zurich (Switzerland) under different seasonal conditions. Within these, f_M(EC) measurements were used for the apportionment of biomass and fossil fuel burning contributions to EC, which showed 6 ± 2%, 12 ± 1%, and 25 ± 5% fractions for biomass burning during summer, springlike, and winter conditions, respectively. With an average EC/OC emission ratio of 0.16 ± 0.05 for residential wood burning, we determined the fractions from biomass-burning, fossil fuel, and natural biogenic emissions for OC to be ~41%, ~32%, and ~27% for winter and ~10%, ~31%, and ~60% for summer, respectively. Thus $^{14}C/^{12}C$ determinations of different carbon fractions yield an assessment of the major emission sources of carbonaceous aerosols. On this basis, regulatory measures can be designed with higher accuracy compared to presently available model calculations.

[28] **Acknowledgments.** This work is supported by the Swiss National Science Foundation (projects 2169-061393.00 and 200020-103605.00) as well as the Swiss State Secretariat for Education and Research (SER) in the framework of the EC project Atmospheric Composition Change: a European Network (ACCENT). We thank C. Hüglin, S. Reimann (EMPA), and MeteoSchweiz for providing meteorological and NABEL data, R. Quartier (BUWAL) and H. Sommer (AWEL Zurich) for PM_{10} emission inventory estimations, S. Andreani-Aksoyoglu (PSI) for CAMx4 calculations, S. Brütsch (PSI) for potassium measurements, R. Fisseha (PSI) and V. Samburova (ETHZ) for their help in the field work, and M. O. Andreae (Max Planck Institute for Chemistry) for his assistance with the reference list for the EC/OC emission ratio. We are grateful to PSI and ETHZ, which jointly operate the Zurich AMS facilities.

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